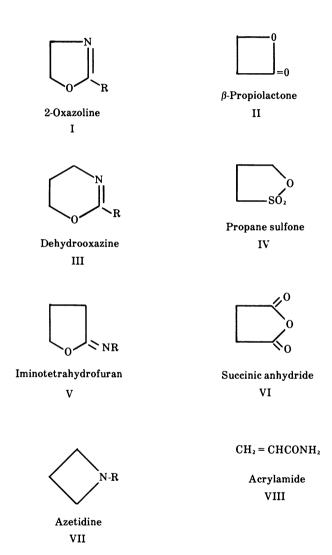
Difficulties of Forecasting Health Implications

by Hans L. Falk*

I was planning to ask the audience a few questions—not what the conference gave to them—for which I have no answers. I thought I could get information about some compounds by inviting these experts but they declined: the reason some gave was that there was nothing as yet to report about health effects.

The first problem, spontaneous copolymerization, is not acute but probably will arise in the future. Today this process is still too expensive for production and only the developers of these products at this stage are interested in their properties, but the principles of formation of alternating copolymers by spontaneous copolymerization (1) are interesting. I don't know details about the products, but the reason I raised the question is that most of the compounds II, IV, VI, VIII, except for the acrylamide (which is neurotoxic) are carcinogenic alkylating agents. If the process materialized into full industrial usage, we could have a potentially serious health hazard. The odd-numbered compounds (I, III, V, VII) with which the alkylating agents react to form polymers. could be replaced by the bases of human DNA. That would create carcinogenic or mutagenic hazards. Could anyone here predict that this is not likely to be a process of the future, that it will not be developed, or that it could be "handled with care" because of the recognition that this would be an occupational hazard?

Another type of polymer is the class of polyorganophosphazenes (IX) which are formed from simple inorganic starting materials, namely, ammonium chloride and phosphorus pentachloride, which form a trimer which is then reacted with organic groups such as amines, to give a whole variety of either crosslinking or straight-chain polymers which may have properties of interest to industry (2).



These polymers contain the N-P chain. At this time, no one was willing to talk about health hazards of these products. This may be because I asked the question: "Would you be willing to talk about the environmental and health impact of these new polymers if they became economically feasible?" The answer was: "No! nothing is known about their impact at this time."

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$$\begin{array}{c}
RO & OR' \\
--- N = P - - ---
\end{array}$$
or
$$\begin{array}{c}
RHN & NHR' \\
--- N = P - - ---$$
IX

The next topic deals with degradation inhibitors and photosensitizers. This brings up a question that is finally reaching the limelight: namely, how do we decompose some of the polymers that we want to destroy? The major problem is that the the same time that we are looking for new techniques for decomposition of polymers we are developing new agents to prevent decomposition from taking place. A recent note (3) describes a new chemical, a nickel compound (Mark 1306 A and B) (no structure given), that is an effective absorber of ultraviolet light, sufficiently stable so that one need no longer worry anymore about environmental degradation of the product.

My interest is to move to environmental degradation, i.e., in the opposite direction. Photosensitizers are compounds which trigger decomposition of polymers on exposure to light; they include brominated or chlorinated styrenes, nitroaromatics, benzphenone, and methyl ethyl ketone. Only one seems to be in production at this time: it has the trade name Sty Grade, but I do not not know its chemistry. Perhaps someone can tell me. The possible use of these photosensitizers by incorporation into some polymers is being worked on quite successfully (4). However, for instance, the addition of brominated or chlorinated styrenes to the polystyrene may introduce toxicity that is not taken into consideration when styrene polymer toxicity is reviewed. We may have similar difficulties with other photosensitizers added to facilitate degradation. Adding chemicals that will trigger degradation may give us new compounds to worry about that may impinge on the environment as a result of facilitating degradation. I do not know all the breakdown products of these compounds after they have been activated by ultraviolet light. It is true that they could lose the energy and return to their ground state, but other products are likely to be formed. Perhaps we have reached a situation similar to that discussed for flame retardants: so many different compounds are formed on pyrolysis that to know all the degradation products of the photosensitizers, we could have a conference just on that issue. The photosensitizers may become health problems—not just because of their use for degrading plastics—but also for degrading pesticides.

Blowing agents are chemicals used to generate a gas during the polymerization reaction to produce products with foamy properties. Several gases could be used: CO2, air, or other chemicals that vaporize readily. The best choice would be an inert chemical that is harmless before, during, and after polymerization and which liberates an inert gas. All of the compounds chosen as blowing agents (X-XVII) give mainly rise to nitrogen or carbon dioxide and are considered safe for those using these airy rigid or elastic plastic materials. The only aspect that is of concern is that all of these blowing agents look like dangerous chemicals. In the process of making an inert gas, we use what seem to be rather toxic starting materials. Of course, we also have to realize that besides the nitrogen gas, residues of breakdown products remain. The residues consist of a variety of products which are considered of little harm. They seem to be neither toxic nor to affect the qualities of the products.

Before these compounds got into use, toxicity tests were carried out on some of the compounds X-XVII, and all of them were subsequently used, which is surprising. Azodicarbonamide (X) would react with many chemical groups. It was used as a flour-maturing agent. It decomposes to ammonia, carbon monoxide, carbon dioxide, and nitrogen; but when it is intact, it is toxic to the thyroid (5). Azobisisobutyronitrile should break down to nitrogen and more complex compounds. I do not know whether the breakdown products include cyanide: I did not find data on its toxicity in the literature. The next compound, diazoaminobenzene, was tested for carcinogenicity in several laboratories and was reported in 1935 and 1947-48 to be carcinogenic. Confirmation should be attempted. Compound XIII, dinitrosopentamethylenetetramine, was the one that started our interest in this problem, because one might have suspected that this component might be a carcinogenic nitroso compound. The literature taught us differently. It is not carcinogenic, as shown in three separate studies carried out in independent laboratories (6-8). The next one is dimethyl dinitrosoterephthalamide. For the use of this compound, directions are given regarding the pH at which it must be handled because it may give rise to diazomethane, a rather hazardous alkylating agent. Under proper handling conditions, however, this would not occur. Compounds XV-XVII belong to the group of hydrazides; they also give rise to nitrogen and are used as blowing agents. They leave complex residues. The toxicity of the starting materials is not reported in the literature.

Azodicarbonamide

 \mathbf{x}

$$\begin{array}{c|c}
N \equiv C & C \equiv N \\
CH_3 & | & | & CH_3 \\
CH_4 & CH_5 & CH_7
\end{array}$$

Azobisisobutyronitrile

ΧI

$$\begin{array}{c}
 & \text{H} \\
 & \text{N=NN}
\end{array}$$

Diazoaminobenzene XII

$$\begin{array}{c|cccc} CH_2-N - CH_2 \\ & | & | & | \\ ON-N & CH_2 & N-NO \\ & | & | & | \\ CH_2-N - CH_2 \end{array}$$

Dinitrosopentamethylenetetramine XIII

 $\label{eq:continuous} \mbox{Dimethyl dinitrosoterephthalamide} \\ \mbox{XIV}$

$$NH_2NH \cdot SO_2$$
 \longrightarrow $O \longrightarrow$ $SO_2NH NH_2$

 $p,\,p\,-{\rm Oxybisbenzenesulfonylhydrazide}$

XV

p-Toluenesulfonvlsemicarbazide

XVI

Benzene sulfonylhydrazide

XVII

Many other relevant topics were not discussed. Only little mention was made of plasticizers. Dr. Piver could have discussed stabilizers, as their use and toxicity was one of the topics he had reviewed (9). We were interested in the various stabilizers that serve this purpose. They and their reaction products can be leached from the plastics together with plasticizers and other components like unreacted monomers.

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